

Chapter 1

Equilibrium Thermodynamics

The second law giveth, and the second law taketh away.

E.D. Schneider & D. Sagan

You all know how powerful and varied are the effects of which steam engines are capable; with them has really begun the great development of industry which has characterised our century before all others.

Hermann von Helmholtz

According to the National Aeronautics and Space Administration (NASA), the year 2010 confirms a trend, which has seen a relentless breaking of global temperature records over the past decade, setting another one by matching 2005, the previous hottest year on record. Despite the recent minimum of solar irradiance, which would normally produce a cooling tendency, a recent NASA paper chooses to state quite uncompromisingly that:

We conclude that global temperature continued to rise rapidly in the past decade
and

there has been no reduction in the global warming trend of 0.15-0.20 °C/decade that began in the late 1970s.

This will not be lost on anyone, who has lived through, or taken an interest in, the unusually harsh and widely reported climatic events of 2010. From the massive rains in Pakistan, China and Iowa in the US, the drought, heat and unprecedented fires in Russia and western Canada, to the ‘biblical floods’ in Queensland, Australia, the evidence is stark, that year by year some part of the planet experiences weather of unprecedented severity. Although it is, perhaps, scientifically presumptuous to do so, it is hard not to conclude that these natural occurrences, which are obviously perilous for the affected human communities, indicate that the global warming trend is beginning to influence current weather patterns on planet Earth. It also seems that the most recent manifestations may be providing clear hints of impending danger for the myriad species, which inhabit this formerly safe haven in pitilessly cold and empty space.

It is the aim of this book to probe and identify the causes of this phenomenon, and to achieve this we shall need to construct a diagnostic capability grounded in the science of thermodynamics, which underpins the evolution of energetic activity in Earth’s biosphere. This we shall do in the later sections of this chapter and in [Chap. 2](#). But before we embark on this task, a brief reminder of the genesis of the ecological deterioration which faces the planet is perhaps apposite.

1.1 Fossil Fuels: A Curse or a Benefit?

Sophisticated and elegant scientific analysis techniques have enabled the recording of many aeons of the climate history of Earth. It is done by measuring, the concentrations, the proportions, and the characteristics of gas molecules trapped within 1,000 to 3,000 m long ice core proxies, extracted mainly, but not exclusively, from the ice sheets covering Antarctica and Greenland. For all sorts of technological and mathematical reasons, to be explored later, this type of record cannot provide definitive values for the average global temperature in the distant past. Nevertheless, the temperatures, inferred from the proxy data, extracted from a multiplicity of sources, display trends which are consistent, predictable and repeatable over time intervals which span millennia. In the interglacial periods, temperatures were much as they are now, while in the ice ages they could sink to 8–10°C below today's level. The record shows that temperatures have never been too low, or too high, to be inimical to life—as we would expect since we are still here! This is despite the fact that over these aeons the sun has been getting hotter, as the young star ages. But because of the earth's 'biotic' thermostat, provided by the rich biodiversity of the ecosphere, a thermodynamic equilibrium has been maintained, which has been and still is conducive to life.

However, this stability is changing. About 10,000 years ago a hunter/gatherer species (one of many) now referred to as *Homo-sapiens*, learned the 'trick' of feeding itself by crop farming and animal husbandry. The descent towards ecocide had commenced. Since then the numbers of this species have mushroomed not unlike a virus in a sick animal. By 1900 the population of the globe was estimated to be about 1.65 billion (1,650,000,000), and it is difficult to get away from the fact that, over the intervening years, these rapidly expanding human societies were environmentally destructive, as human throngs are wont to be. From the 'middle ages', or perhaps earlier, populations in the northern hemisphere had managed to lay waste to most of the temperate zone forests mainly for building materials and to construct ships and instruments of war, but also to warm their humble abodes, their cathedrals, and their draughty castles. Fortunately, despite the resultant deforestation, planet Earth was not in any real danger of ecological harm because the population level was still tolerably low.

It also seems safe to say that before the industrial revolution the ecological consequences of mankind's activities remained insignificant due to the fact that their energy consuming technology, was not based on fossil-fuels, was quite limited in capacity and extent, and was rather restricted to local activities which could benefit from power assistance. Much of it was associated with the harnessing of the wind (wind-mills), accessing the power of water (water-wheels) and controlling the power of steam largely generated by burning wood. This early technology was actually of the renewable genre—that is, it employed power which had been extracted from planetary energy sources, such as wind, wood and water flows, sources created by direct sunshine daily warming the planet.

History indicates that some municipal systems for extracting power from wind, rivers and tidal estuaries were surprisingly elaborate and sophisticated in engineering terms even by the sixteenth century [1]. Rather ironically, it has been suggested, that nascent human civilisations, mainly through farming and forest clearing, may have had a small positive ecological impact on the Earth's climate by increasing atmospheric carbon dioxide by just enough to ward off another ice-age [2].

1.1.1 Population Growth

Despite the immaturity of the technology, the benefits to civilisation provided by these early excursions into serious engineering, seem to have coincided with a sudden and rapid growth in population (see Fig. 1.1), in those parts of the world where it appeared. The curve labelled (Indust) shows population growth for the industrial world (USA, Europe, Australia), which by 1800 was powered by fossil-fuels, and this curve, although initially at a low level (~ 170 million), rises faster than the rest of the world from about 1850 to 1950. Around 1950, while the population rise in the industrial world slows and peaks at about 1.2 billion, due in part to high levels of prosperity, female emancipation and availability of effective contraception, the population levels in Asia, South America and Africa 'take off', as these regions belatedly acquire the benefits of technology, but without the social advances. Since 1950 world population has risen much faster than the geometric rate (dotted line), which according to the theory of Thomas Malthus (1776–1834) is the natural response of a species, to improvements in access to food. Notwithstanding his position as an Anglican curate, Malthus regarded with considerable scepticism the ideals of those, who expressed the belief that this phenomenon meant that the lot of humanity would continue to improve into the foreseeable future, by observing that throughout history a segment of every human population has been relegated to poverty. He explained his theory by arguing that population growth generally expanded in times and in regions of plenty, until the size of the population eventually out grew its primary resources, causing hardship. Other species are certainly so restrained, but he omitted to take account of human ingenuity which has enabled humans to 'buck this trend'—until now. He is quoted as saying:

The power of population is indefinitely greater than the power in the earth to produce subsistence for man. Population, when unchecked, increases in a geometrical ratio. Subsistence increases only in an arithmetical ratio. A slight acquaintance with numbers will show the immensity of the first power in comparison with the second.

The Malthusian rate is outstripped in Fig. 1.1 because humans have also discovered how to use energy both to relentlessly improve the efficiency and scale of food production methods, and to secure advances in medical techniques, practices and facilities, and this has further raised birth rates while lowering death rates.

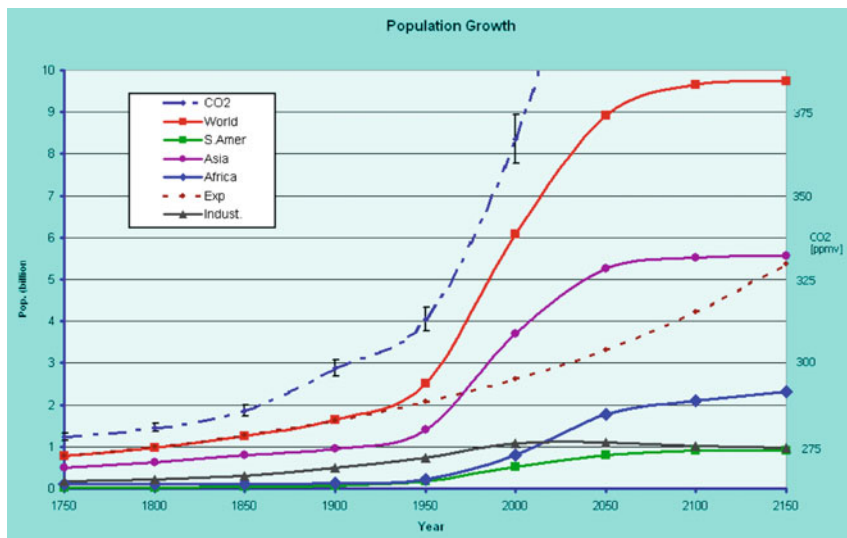


Fig. 1.1 Population growth (actual + projected) between 1750 and 2150 and measured global CO₂ growth over the same period (IPCC)

Needless to say, the growing population has made, and is making, increasing demands on the planet, as Malthus predicted, because more and more communities are seeking access to the ‘fruits of technology’. Unfortunately the primary energy source for this burgeoning desire for the economic advances provided by technology has been fossil fuels, rather than renewable power. From an ecological perspective, the rapid withering of renewable technology has been unfortunate, but perhaps inevitable. The ecocidal expansion of CO₂ in the atmosphere, which has accompanied industrial expansion founded on energy from fossil fuels, is shown as a blue chain-dotted curve in Fig. 1.1, for which the right hand scale is applicable. The correlation with population growth is clear. In fact, it is so irrefutable, that to suggest, as some do, that the problem of accumulating carbon dioxide in the atmosphere is not of anthropogenic genesis, surely verges on the perverse. The recently coined term ‘ecocide’ provides a cynical yet powerfully descriptive word for mankind’s apparent drift towards catastrophic climate change.

1.1.2 Technology Powers Civilisation

The history of the spread of the human species over the land area of planet Earth is principally a story of the emergence and expansion of civilisation, although at very unequal rates in different parts of the world. Nevertheless, throughout the narrative, it is not too difficult to discern, even with the merest acquaintance with our human tale, that ‘progress’, however one chooses to interpret or define it, was

everywhere a fluctuating affair. It still is. The ‘ups and downs’ in human societal development took many forms and guises, and was influenced by many events. Arguably a consistent thread of economic progress can be perceived there in, although not without some difficulty, because it is intermittently impeded by the enactment of some major dramas, which have featured in the journey of our species from hunter/gatherers to, for some, modern urbanised sophisticates. These have been at times, as is well known, quite traumatic and destructive.

Notwithstanding the reversals, it is quite hard, in reading the history [1, 3], not to reach the conclusion that much of civilisation’s recent economic advance can be ascribed to a seemingly unending flow of innovative technological developments, powered by coal, oil and natural gas. Technology has certainly helped to satisfy some basic needs for humans such as immunity from the effects of bad weather, partial protection from severe climatic events, security from predators and reliability of food supply. Also for some, it has permitted time and space to pursue and acquire better health, education, political freedom, participation in democracy, time for family and friends, and creative expression. But the term ‘civilisation’ seems to be too grand a description for what humanity is haphazardly and incoherently constructing. It seems that we are ‘good’ at assembling financial structures to power national and global economies, at designing and building infrastructure in our towns and cities and at manufacturing the artefacts which make existence tolerably comfortable, but the term ‘civilisation’ suggests that ‘quality of life’ should be part of the mix. Unfortunately, except for a very few, namely the rich and powerful, recognisable advances in quality are hard to identify. For the vast majority of the global population, in those parts of the world considered to be ‘civilised’, the hard earned prizes of freedom and democracy, where they are available to them, are generally unappreciated and seemingly of little interest to many, as they have become seduced by the cult of consumerism and a desire for instant gratification. As Jonathan Porritt [4] has suggested, humans today are on a ‘hedonic treadmill’, which is:

the great driving force of modern capitalism, with governments compelled to condone and even exhort ever higher levels of consumption in order to keep their tax revenues flowing, with business able to deploy ever more sophisticated marketing to reinforce a sense of permanent dissatisfaction on the part of individual consumers, and consumers themselves (for lack of evidence to the contrary, let alone any serious Plan B) seemingly persuaded that consumption as a proxy for living is probably the best thing on offer. Even though it leaves them no happier or more fulfilled, even as levels of personal consumption move relentlessly upwards.

Other groups within the ever scurrying, and consuming multitudes, aggravate this depressingly uncivilising trend, by drifting unthinkingly towards inappropriate and unhelpful fundamentalist and coercive religions. These organisations tend to have little difficulty in tolerating the notion that the masses can be pacified by means of a plentiful supply of ‘opiates’, in the form of consumer goods. With ever increasing numbers of humans on the planet demanding that their materialistic consuming instincts should be assuaged, and with governments of all persuasions making every attempt to gratify them.

This is not about to change any time soon, since, as Porritt correctly observes:

Children the world over are brought up on the same evolutionary account: that it was humankind's capacity to use tools that first helped us to establish our ecological niche, and that this slowly evolved into an increasingly powerful ability to assemble raw materials extracted from nature into objects, machines, buildings and so on. For most of our short history, this conversion process (from natural capital into manufactures capital) was relatively modest, localised and mostly low impact as far as the environment was concerned. But from the mid-18th century onwards, the Industrial Revolution transformed the balance of that relationship between the biosphere and the technosphere. The availability of cheap fossilised fuels from the middle of the 20th century onwards has further increased the dependence of human beings upon countless different sources of manufactured capital

Nevertheless it is clear that the current direction of 'civilisation' has the potential to render the planet uninhabitable in the not too distant future, because of uncontrollable environmental degradation. Humanity needs to articulate a 'goal' for its technology based civilisation. The 'project', including economic activity, surely has to follow a sustainable path. Unfortunately, neither the formulation nor the communication of new guiding principles for the future long term occupancy of the planet have been given serious attention, as far as I am aware, although this may be changing [4]. Any coherent religious meaning to 'human progress', which may have been posited in the past, is becoming more and more spurious in this modern world of over-population and planetary squalor for which most religions, with their immanent dogmas, which urge and facilitate population expansion rather than the opposite, have no answer. Of course, those propagating ideas of 'rapture' are totally unconcerned at the possibility of the habitable planet going 'down the tubes'. They will be elsewhere! In "An Angel Directs the Storm", M. Northcott [5] quite clearly and concisely identifies this rather scary evangelical phenomenon, which has emerged in the USA, in the following quotation:

Pre-millennialists believe they are living in the end time, and it is an era of growing lawlessness and dreadful wars which threaten to extinguish human life on Earth. Only after these events will Christ return to inaugurate a literal 'thousand-year reign of peace', which millennialists believe is predicted in the Book of Revelations. Pre-millennialists also believe that true believers will be 'raptured' or plucked off the planet by God before the Great Tribulation, so that only those 'left behind' will have to face the terrors of the end time - the last great conflagration of Armageddon, or World War III, which happen as a result of the escalation of crisis in the Middle East.

But for most of mankind a form of 'civilisation' which appears to involve pursuing economic progress, almost exclusively for 'wealth' creation of the material kind, to feed 'consumerism', continues to be the long term goal and little else seems to be of concern. Certainly while this is the case, scientists and engineers will continue to invent, and hence keep the process going. A good example is the evolving scientific discipline of nanotechnology which promises, in addition to applications with serious intent, all sorts of shiny new goodies and gadgets for the consuming masses in the not too distant future. All that the purveyors of technology seek are reliable sources of sponsorship. The moral or ethical implications, of the use or misuse of their discoveries and inventions, tend to bother only a very

small proportion of the technological ‘whizz-kids’. Some, those very few attached to science and engineering institutions may perhaps express disquiet, but their influence is essentially negligible. As a result, in a world which has largely espoused global capitalism, it is clear that unrestrained consumerism or materialism is not a feasible option. It is certainly not a sensible aspiration, for one simple and over-riding reason. Since the global economy cannot be decoupled from the environment, and by extension the ‘real’ world, and since civilisation’s gains through economic growth are arguably dependent on technology powered by fossil fuels, endless ‘progress’ has the potential to be very dangerous for the ecological health of the planet, as we are now beginning to discover.

1.1.3 Economic Misgivings

Long before the ecological ramifications of the current global economic system became known, wise heads were proffering warnings of a downside to unremitting economic progress. By the system we mean market capitalism, which now holds sway over most of the globe. In 1848, John Stuart Mill [6], an eminent philosopher and political theorist, who was born in London to Scottish parents, is quoted as saying, in his “Principles of Political Economy”:

I cannot... regard the stationary state of capital and wealth with the unaffected aversion so generally manifested towards it by political economists of the old school. I am inclined to believe that it would be, on the whole, a very considerable improvement on our present condition. I confess I am not charmed with the ideal of life held out by those who think that the normal state of human beings is that of struggling to get on; that trampling, crushing, elbowing, and treading on each other’s heels.... are the most desirable lot of mankind.... It is scarcely necessary to remark that a stationary condition of capital and population implies no stationary state of human improvement. There would be as much scope as ever for all kinds of mental culture and moral and social progress; as much room for improving the Art of Living, and much more likelihood of its being improved.

This is unbelievably prescient, yet the dash for growth in the intervening years, suggests that few economists can have bothered to read Mill’s output. That such warnings have been regularly and ignorantly dismissed by mankind is clear from observations such as this example, by Athanasiou [7]:

Mitsubishi embodies to an extreme degree the fundamental process that sets the modern world apart from its predecessors. Our time - to use words the economic historian Karl Polanyi wrote fifty years ago - lies after the “Great Transformation”, in which “the notion of gain” so overcame the social framework within which it was once embedded, and by which it was restrained, that “human society” was turned into “an accessory of the economic system”. We live, as Polanyi put it, within the “stark utopia” of the “self-regulating market”. Finding ourselves within a long movement of social and ecological decay, it is not difficult for us to appreciate his 1944 warning against economic forces so unrestrained that “the laws of commerce” come to seem “the laws of nature” - and consequently “the laws of God”. As for Polanyi’s conclusion that “a self-regulating market” cannot exist for any length of time without annihilating the human and natural substance of society”, what is it if not an early statement of a now open secret?

Sixty years later the economic system still powers ahead, with an occasional recessionary stumble, as if the planet had infinite capacity to absorb all mankind's foolhardy misuse and abuse of its natural resources. Growth based on the combustion of increasingly copious volumes of fossil fuels to feed rampant consumerism seems to have become the *raison d'être* of modern life. Civilisation has become equated with economic progress, and consequently, it is difficult for 'rich world' populations not to infer that unless there is growth economically we die! Yet historians will likely view the current headlong rush for growth and prosperity as merely a 200 year 'blip' on the graph of human evolution; life without any prospect of material advancement has, in fact, been the historical norm. We shall return to this issue in [Chaps. 5](#) and [6](#).

1.1.4 The Power of Steam

The story of the technology, which has underpinned civilisation's physical development, is largely a saga of rapidly expanding exploitation of the power of the sun—but not, unfortunately, the power gifted by current sunlight, but power derived from 'ancient sunlight' in the form of the energy stored in the fossilised deposits of the flora and fauna of primordial forests. Inevitably, given human nature, it is also a tale of the use and misuse of this power. In the sixteenth and seventeenth centuries, in several parts of the world, but particularly in Britain, it was apparent that an agrarian revolution was under way, and that in tandem, an industrial revolution in the textile industry, in coal mining, in shipbuilding and in the manufacture of iron, tin and glass was taking root. A mercantile system was in place to facilitate internal markets and global trade [\[3\]](#). Consequently the social, political, commercial, economic, manufacturing and technological conditions were ripe for a massive expansion of industry including food production. "Capitalism, with coal, iron, and engineering enterprise, gave rise to industry, and in the end to the forces, which led to modern technological civilisation" [\[3\]](#). The iron and coal were required to construct and to energise powerful engines to turn the wheels of industry, which was thereby, unleashed from the limitations of water and wind power. But in order to mine coal and produce iron in sufficient quantities to meet demand it was necessary for the mines and the iron works themselves to have access to the power of steam.

The first steam pumping-engine was invented [\[3\]](#) by Thomas Newcomen (1663–1729). By using jet condensation of steam in a cylinder, low pressure was generated in the space above a piston. Thus atmospheric pressure was enough to move the piston and do work on a beam attached to a pump. These engines could be large, as anyone who has visited an industrial museum will know. The working cylinder could be as much as 2 m in diameter with a 3 m stroke. Engines of this type were adopted widely in industrialising Europe.

The Newcomen steam powered pump provided the solution to a major obstacle which was impeding the development of coal mining. The extraction of water from

mines was becoming extremely expensive, if not impossible in some cases. That the pumping of water from deep mines could be done much more economically and effectively with the Newcomen engine was evident from the fact of its widespread adoption.

With the increasing availability of coal, came the growth of iron making. This skill had come to Western Europe and Britain with the Romans and was used mainly to forge weaponry. By the eighteenth century there was a shortage of wood for making the charcoal which was essential to the smelting process. In Britain, the countryside had largely been denuded of its sea-to-sea forests to make way for farming and to provide building materials for growing towns and cities and for shipbuilding. Iron was being imported from Sweden. Smelting with coal, in the form of coke, appeared around 1600, and by 1709 an iron works at Coalbrookdale in England was producing about 5–10 tons of cast iron per week. At its peak Coalbrookdale employed 16 steam engines to service eight blast furnaces, nine forges, rolling mills and foundries. A mutually dependent trio of steam power, coal and iron had been created. It would be the pivotal motivator of early industrialisation, and in particular the industrialisation of the textile industry.

The process was helped along by James Watt (1736–1819). This quintessential Scottish engineer was initially an instrument maker in London, before moving to Glasgow to become a laboratory technician at the university there. While there, he attended lectures on heat and was mentored by another Scot, Joseph Black (1728–1799), a physician, physicist, and chemist, known for his discoveries of latent heat, specific heat, and carbon dioxide. He is credited with being a founder of thermo-chemistry and developed many pre-thermodynamics concepts, such as heat capacity. Watt was given the task of repairing a model of a Newcomen engine and while doing so he determined how to improve its efficiency. His genius was to provide a separate condenser so that the expansive power of steam could be used in addition to the vacuum power used by the Newcomen engine. It led to push/pull motive power. Watt's proposed design was three to four times more efficient than a Newcomen engine, and as a consequence he became a rich man in supplying it to the coal mines, with the help of his mentor Black and with the entrepreneurial guidance of John Roebuck and Matthew Boulton, both industrialists. By 1800 there were about 500 Boulton/Watt steam engines in Britain in mines, iron works and textile mills. In the United States industrial expansion based on steam was equally rapid. Between 1781 and 1790 the number of private companies or corporations involved in bringing about the 'revolution' in that part of the world grew from 33 to 328 [8].

It is interesting, and relevant only insofar as it illustrates Watt's practical engineering skills, to recount that in 1783 Watt is said [9] to have: "tested a strong horse and decided it could raise a 150 lb weight nearly 4 feet in a second. He therefore defined a 'horsepower' as 550 foot-pounds/s." How precisely the test was performed is not recorded. Nevertheless the definition still persists, although it is hardly used any longer in our modern world of SI units.

By the end of the nineteenth century, the opportunities which seemed to be offered by the advent of steam power, encouraged scientist and engineers

empowered by entrepreneurs, to envisage the spread of industry into many activities beyond coal, steel and textiles. Sadi Carnot (1796–1832), a brilliant French applied scientist and engineer who pointed the way to a theory of thermodynamics, is quoted as saying [3] that: “steam engines will afford to the industrial arts a range the extent of which can scarcely be predicted, and that they can even create entirely new arts”. The industrial revolution had begun and the potential to seriously damage the ecology of the planet had been incubated.

1.2 Heat Demystified

Before 1800, science was at an elementary stage of evolution, so that even the very nature of heat was unknown to the early engineers endeavouring to comprehend and utilise the power of steam. Today, most people with just a smattering of school science would have little difficulty fathoming the basic thermodynamics of heat engines. Despite their difficulties, however, highly practical engineers such as Newcomen and Watt, scarcely seems to have been delayed or deflected in their endeavours, as we have seen. Their efforts had initiated the steam revolution. This was perhaps fortunate for the human species which had begun to grow uncontrollably, but in retrospect it has hardly been wholly beneficial for the planet!

For ‘pure’ science, on the other hand, heat was undeniably a conundrum. Rather surprisingly, when viewed from a modern perspective, it was actually considered, by the scientists of the day, to be a form of chemical element. A. L. Lavoisier [10] (1743–1794) who is often described as ‘the father of chemistry’, certainly judged it to be so [11]. In fact he regarded heat as a fluid which he termed the caloric. The caloric clearly seemed to have troubled Carnot [12], who in expressing confidence, that he had established a fundamental law relating to the optimal efficiency of heat engines, makes the following perceptive observation in 1824:

The fundamental law that we have proposed seems to us to require ... new verification. It is based upon the theory of heat as it is understood today ... (whose) foundation does not appear to be of unquestionable solidity.

Today, the *Carnot engine* is defined as an engine which operates with optimum efficiency between a high temperature reservoir and a low temperature sink. A heat engine employing an ideal gas and working between two temperatures is termed a Carnot machine. If these temperatures are T_{low} and T_{high} in Kelvin, then the optimum efficiency (η) is given by:

$$\eta = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} \quad (1.1)$$

As such it is an ideal engine, which means that it operates by using only reversible processes. The engine itself is therefore reversible, acting as an engine or a refrigerator. The efficiency of the Carnot engine, provides a measure of the maximum possible efficiency of any real heat engine.

1.2.1 Conservation of Energy is Established

However, by 1850 the caloric theory was totally undermined by three scientists largely working independently. Generally acknowledged to be among the ‘giants’ of thermodynamics, they were R.J. Mayer (1814–1878), J.P. Joule (1818–1889) and H.L.F. Helmholtz (1821–1894). By establishing the now axiomatic rule, that at all times energy is conserved, it became impossible to treat heat as anything other than energy, and as a consequence they were able to dismiss the caloric to history. Mayer is quoted as saying [10], somewhat unscientifically, “Let’s declare it, the great truth. There are no immaterial materials”. Of course today, the law of conservation of energy is usually referred to as the first law of thermodynamics. It was arguably the greatest scientific revelation of the nineteenth century. Today, it is known that energy and mass are interchangeable, as expressed by Albert Einstein’s famous equation, and consequently scientists have now integrated mass into the statement of the first law.

1.2.2 Nascent Formulation of Second Law

Something was still missing, however. The law of conservation of mass/energy does not expose the true nature of heat, and what it means physically for a substance to be hot. So, if heat was energy, what were the internal processes within a material that could explain the difference between a ‘hot’ substance and a ‘cold’ one? This step was made by R.J.E. Clausius (1822–1888) and led to the formulation of the second law of thermodynamics. The developments which appear to have intrigued and influenced Benoit P.E. Clapeyron (1799–1864), Clausius, and later William Thomson (Lord Kelvin—1824–1907), emanated from the work of Carnot on the optimum efficiency of a heat engine and in particular on the Carnot function, which was key to quantifying an optimum for any given engine [11]. Carnot, who died at thirty eight, was unable to provide the answer. The outcome of research, conducted by Carnot’s successors over several years, was the establishment of the absolute temperature scale (now named after Lord Kelvin), and the demonstration that in this scale the Carnot function is the reciprocal of temperature. This led to the realisation that a hot body must possess an internal energy and that this energy was associated with vibrating molecules. In other words heat is a form of kinetic energy.

The end result was the observation, attributed to Clausius, that: “heat cannot pass by itself from a colder to a warmer body”. This would be like a moving pendulum, when striking the bob of an identical pendulum hanging from a nearby suspension point, delivering to this second pendulum more than its own maximum kinetic energy. If the process was serially repeated for three or more pendulums, the swing amplitude of each succeeding pendulum would get larger and larger, which is patently impossible, as anyone will know who has watched the annoying,

yet ubiquitous kinetic ornament, comprising five (usually) steel spherical bobs suspended from a frame. The swing motion gradually decreases and dies out, in accordance with the first and second laws.

1.2.3 Entropy Defined

The phenomenon of heat decay has become to be known as entropy (a word coined by Clausius), and the observation is a statement of the second law of thermodynamics. It really gives expression to a common sense principle that no process in nature, not just the physical, such as heat engines, but also chemical, biological and informational, can proceed without some sacrifice in energy. So while the first law informs us that the total quantity of energy in a closed system will be conserved, the second law addresses the quality of the energy, and how it inevitably becomes degraded and less capable of being converted into useful work. As Steven Weinburg [13] graphically puts it, the second law “forbids the Pacific Ocean from spontaneously transferring so much heat energy to the Atlantic, that the Pacific freezes and the Atlantic boils”.

In the irreverent style of the youthful, the first law and second laws, two supreme and far reaching statements from science, have been reduced by science students succinctly and not inappropriately to the following [11]. In the physical world that we humans inhabit ‘you cannot win’ (first law) and more importantly ‘you cannot even break even’ (second law). These laws are really a statement of the fact that the planet, the solar system and perhaps even the universe, are finite. This has been known now for almost 160 years. Yet, here on Earth, human economic developments are still (in 2009) predicated on the possibility that the finiteness of the planet and the limits of mother-nature can be circumvented, as if human beings and their activities are not part of the natural world. For example, the eminent American economist, Milton Friedman [14] is said as having opined quite recently:

Most economic fallacies derive from the tendency to assume that there is a fixed pie; that one party can gain only at the expense of another.

The fact of mankind’s confinement on a *finite* planet, on which all natural processes are governed by the laws of thermodynamics, would rather seem to make fallacious, Friedman’s contention! It could only ever have been approximately true when human population could be counted in millions rather than billions. As fellow economist E. Cook has noted, rather undermining Friedman’s view:

The concept of limits to growth threatens vested interests in power structures; even worse, it threatens value structures in which lives have been invested. Abandonment of belief in perpetual motion was a major step towards recognition of the true human condition. It is significant that mainstream economists never abandoned the belief, and do not accept the relevance to the economic process of the second law of thermodynamics; their position as high priests of the market economy would become untenable did they do so [15]

Seth Lloyd, a professor of mechanical engineering at the Massachusetts Institute of Technology, who is known for contributions to quantum computing, was even nearer the truth about the importance of the second law, when he made the comment that:

Nothing in life is certain except death, taxes and the second law of thermodynamics.

To persistently believe that modern global financial systems can be decoupled from the ‘real’ economy, in a real world which has to operate in accordance with the laws of thermodynamics, is quite clearly ‘moonshine’ as we shall see in [Chap. 5](#). That many economists, rather incredibly still do so in 2010, is attested to by the global credit crunch of 2008.

1.3 Thermodynamics: Laws Zero to Three

1.3.1 *The First Law*

The establishment of the first law of thermodynamics, or the law of conservation of energy, grew out of scientific pondering on the idea of a ‘perpetuum mobile’, or ‘perpetual motion machine’. Perpetual motion appears to have intrigued scientists and engineers in the nineteenth century, firstly since it seemed to defy common sense, and secondly since it was acknowledged that a demonstration of its impossibility would go a long way towards establishing that energy conservation represented a fundamental tenet of nature. Actually, even before the input of Helmholtz, the irrationality of the perpetuum mobile was slowly becoming accepted, especially in the case of energy at the macroscopic or human scale; that is kinetic energy, potential energy and elastic energy. This macroscopic law was gaining recognition under the banner of the law of conservation of mechanical energy [11].

Helmholtz’ contribution to the debate was to realise that the internal energy of the materials, from which a macroscopic system might be constructed, merely made it much more complicated in energy terms. He is recorded as observing [11]:

what has been called ... heat is firstly the ... life force (kinetic energy) of thermal motion (of the atoms) and secondly the elastic forces between atoms. The first is what was hitherto called free heat and the second is latent heat.

Despite this additional complexity he was moved to observe that the impossibility of the perpetuum mobile should still apply. While the argument, that energy is conserved, had been accepted for elaborate macroscopic arrangements, provided that friction could be ignored and collisions could be assumed to be inelastic, Helmholtz argued that it must equally be true for such systems, even when friction is finite and collisions are elastic, and that this could be done by broadening the scope of the law to include the potential and kinetic energies of vibrating atoms. He averred that friction and elastic collisions simply have the effect of transferring

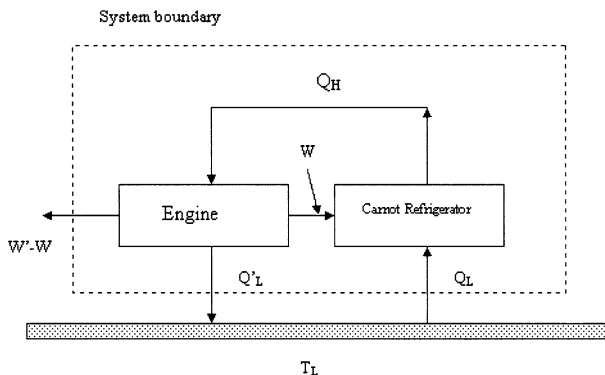


Fig. 1.2 Carnot efficiency demonstration

energy at the microscopic scale, into energy at the macroscopic level. The concept was reported to the Physical Society of Berlin in 1847, under the title ‘On the conservation of force’. At the time ‘force’ was the term used to identify what we would now define as energy. The presentation begins with the sentence [11]:

We start from the assumption that it be impossible - by any combination of natural forces (energy)—to create life force (kinetic energy) continually from nothing.

The first law of thermodynamics had been established.

1.3.2 The Second Law

The statement of the second law of thermodynamics (see above) formed by Clausius, is much too vague to form a scientifically workable law. Clausius’ initial steps towards a more robust formulation, involved giving deep consideration to what happens if two reversible Carnot machines, working in the same temperature range, compete (see Fig. 1.2).

One is presumed to be operating as a heat engine, producing mechanical power (W') from heat, and the other as a heat pump or refrigerator, employing mechanical power (W) to expand the working gas thus cooling it. The mechanical power from the heat engine is used to drive the refrigerator while the heat (Q_H) extracted from the refrigerator powers the heat engine. If the engine is assumed to be more efficient than the Carnot refrigerator, then $Q'_L < Q_L$ and $W' > W$. But this implies that we have a system which is producing net work ($W' - W$) from a single reservoir at temperature T_L , and this contravenes the second law. Therefore it is not possible to create an engine with more efficiency than the Carnot maximum. Perpetual motion would also require one or other machine to be more efficient than the Carnot optimum in converting heat to mechanical power or vice versa, and consequently it is equally unachievable. That the efficiencies of both

machines are equal [11] in such a system, had already been demonstrated by Carnot on the basis of the first law. Also, since nothing in the postulated experiment is said about the working agents or gases he could assert that the efficiency must be independent of the agent used, again confirming the work of Carnot. If one accepts the law of conservation of energy, it must be true that, for a Carnot engine, its efficiency is equal to the heat applied (power in) to the boiler ($Q_{\text{boiler}} = Q_H$) minus the heat (power out) of the exhaust ($Q_{\text{out}} = Q_L$) divided by the heat applied: i.e. $\eta = 1 - \frac{Q_{\text{out}}}{Q_{\text{boiler}}}$. But for a Carnot engine: $\eta = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}$ as we have already seen (eq. 1.1). Hence, the following proportional relationship between heat and temperature ensues; namely that:

$$\frac{Q_{\text{boiler}}}{T_{\text{high}}} = \frac{Q_{\text{out}}}{T_{\text{low}}} \quad (1.2)$$

This equation expresses the important fact that it is not heat that passes through a Carnot engine unchanged, as Lavoisier thought, but the quantity Q/T . This ratio is what Clausius termed entropy (S).

1.3.3 Gibbs Equation

When the definition of entropy is combined with conservation of energy and applied to the case of an ideal gas, an equation results, which is named after J.W. Gibbs (1839–1903) of the University of Yale (for a detailed derivation see Chap. 9). The equation for entropy together with the Gibbs equation (see Chap. 9 Eq. 9.6) has the important consequence that for an adiabatic process, for which no free energy is available, entropy must be positive, since internal energy cannot be negative, and temperature on the Kelvin scale is always positive. Furthermore in time, as the cooling process continues internal heat energy and temperature tend to zero in such a way that their ratio, entropy, becomes a maximum, and all actions cease. In a closed system, for which there is no external source of energy (e.g. the universe perhaps), this implies that its internal energy must dissipate unremittingly. “So the world has a purpose, or a destination—the heat death [11]”. Clausius is reported to have put it this way:

It is often said that the world goes in a circle Such that the same states are always reproduced. Therefore the world could exist forever. The second law contradicts this idea most resolutely. The entropy tends to a maximum. The more closely that maximum is approached, the less cause for change exists. And when the maximum is reached, no further changes can occur; the world is then in a dead stagnant state.

Needless to say this claim caused not a little controversy at the time, from cosmologists to religious leaders [11].

While the Gibbs equation gives a useful indication of the import of entropy in some particular physical scenarios, it fails to provide an objective interpretation of the second law. To do this it is helpful to reconsider the nature of an ideal gas and

the movement of molecules within it. For such a gas, the thermal equation of state developed from the research of Robert Boyle (1627–1691) among others [11] applies. Today, it is generally referred to as Boyle's law, which in words dictates that for an ideal trapped volume of gas the product of its pressure and volume is proportional to its temperature in Kelvin. The law can be stated as follows. The equation of state for all gases under low pressure is:

$$pV = NkT = RT \quad (1.3)$$

where p = pressure (N/m^2): V = volume (m^3): T = temperature (K): k = Boltzmann constant (1.1×10^{-23} J/s K): N = number of molecules in the gas. The universal gas constant $R = 8.314$ J/K for 1 mole of the gas. For such a gas the internal energy associated with the vibrating molecules [11] is given by:

$$U = \frac{3}{2} NkT \text{ J} \quad (1.4)$$

To establish a physical interpretation of the second law in such a gas, a major advance in the mathematical representation of the behaviour of gases was required. This step was furnished by James Clerk Maxwell (1831–1879) and reinforced by Ludwig Eduard Boltzmann (1844–1906). It was obviously known, from the work of earlier pioneers on gas behaviour, that gas pressure was simply a manifestation of vibrating molecules striking the containment vessel walls, thus producing pressure as a result of the change in momentum of each particle. What was not known was the distribution of the velocities of these molecules and how the distribution could change with time—an impossible problem for classical dynamics.

1.3.4 Statistical Interpretation of Entropy

Clearly, it is statistically unlikely that all molecules will have the same velocity even in an ideal gas in equilibrium. The random nature of molecular fluctuations (Brownian motion) had already been demonstrated by Robert Brown (1773–1885) on the basis of microscopic studies of the irregular motion of minute grain particles suspended in a fluid. Maxwell, by simplifying the problem to a gas comprising N molecules, in a volume V , which is at rest as a whole, found a way to make the problem mathematically tractable. He further assumed that the gas was in equilibrium, and was therefore homogeneous, with an isotropic distribution of molecular velocities. A typical electron is supposed to be travelling in the i -direction. A gas of this description will have an internal energy of $U = 1.5 NkT$ J, as demonstrated above. With each molecule having an arbitrary velocity (c_i) with components in the three orthogonal space directions, it can readily be deduced that (see [Chaps. 11 and 12](#)) the fraction of molecules ($D(c_i)$), with this velocity is given by:

$$D(c_i) = \frac{1}{\sqrt{2\pi k_\mu T}} \exp\left(-\frac{E}{kT}\right) \quad (1.5)$$

where T is temperature in Kelvin and E is the kinetic energy of a molecule with velocity c_i . Distributions such as the one above are sometimes referred to as Maxwellian, in acknowledgement of Maxwell's role in the development of a kinetic theory for gases.

In Fig. 1.3, Maxwellian distributions computed for a litre of air, at three different temperatures, are presented. The 'bell shaped' curves are typical of probability distributions and show that most molecules in the gas have low velocities, in the vicinity of $c_i = 0$ where the peak occurs, while only a very small number have velocities which deviate significantly from zero near the base of the 'bell'. The statistical interpretation would be to observe that a high value for D at $c_i = 0$ implies that the probability of gas molecules having velocities close to zero, in all three cases, is much greater than for it possessing rapidly moving particles. When the temperature is lowered from 273 (0°C) to 200 K the probability of molecules having a low velocity rises and vice versa for 'fast' molecules. This is in accordance with common sense expectations. The opposite happens if the temperature rises from 273 to 346 K. That the Maxwell distribution is essentially statistical in nature was known to Maxwell [11] but it was Boltzmann who made most headway in applying probabilistic arguments to the kinetic theory of gases. Needless to say Maxwell had got it right, and the statistical approach led to the same expression for the velocity distribution of molecules in a gas at equilibrium. The exponential term $\exp(-\frac{E}{kT})$ which is the main component of the equation, has become to be known as the Boltzmann factor.

1.3.5 Entropy and Boltzmann

The 'bell' curves depicted in Fig. 1.3 show clearly that for a gas, as the temperature drops, the distribution becomes sharper indicating that more and more molecules are losing kinetic energy and hence velocity. This suggests that, with time, the molecular velocity distribution in an isolated volume of gas diminishes, and hence its temperature falls, in accordance with the second law of thermodynamics. But what is the precise process? In a warm gas, as has already been indicated, the temperature is simply a measure of the mean kinetic energy of its molecules. These randomly moving molecules are continually colliding with each other and with the walls of the containment vessel. Crudely, the situation is analogous to a large number of moving snooker balls on a large flat table with hard cushions. If the distribution of velocities for the balls is Maxwellian then most will be moving slowly or not at all while a few will be rattling around with high kinetic energy. An elementary appreciation of dynamics suggests that these fast moving balls will not remain so for long, due to the slowing process of repeated collisions, whereby their energy is transferred to slower moving balls. The Maxwell distribution for the balls will gradually become 'sharper' reflecting the increasing probability of balls possessing a low or zero velocity.

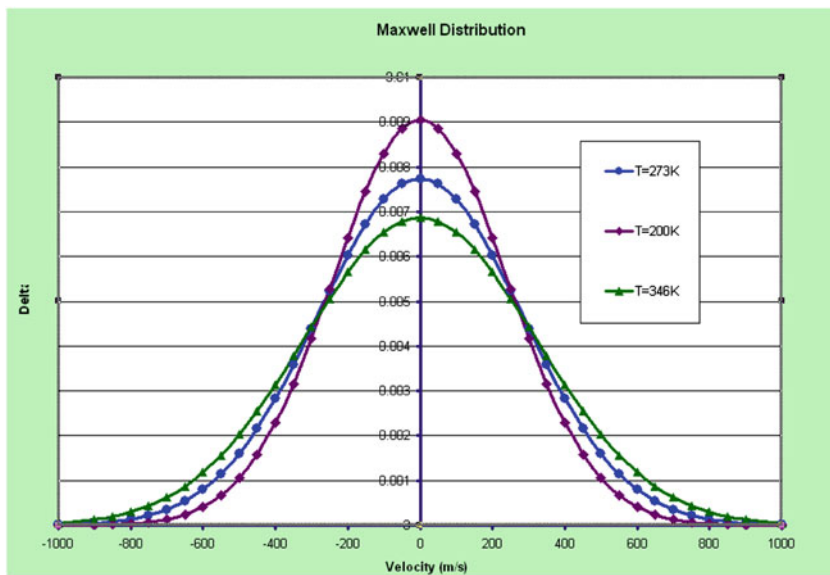


Fig. 1.3 $D(c_i)$ as a function of particle velocity at three different temperatures, for a litre of air for which $k = 1.1 \times 10^{-23}$ J/K: $\mu = 37.8 \times 10^{-27}$ kg

So the Maxwell distribution patently changes with time as a result of slowing collisions, but what are the rules? The problem was addressed by Boltzmann, who realised that statistics provided the only feasible way of accommodating intractably large numbers into mathematical theory. For example, molecules in a finite volume of gas can number many millions or billions, and when dealing with such huge numbers, it was known that statistical averages tend to converge towards macroscopic measurements or macroscopic calculations based on conventional equations. For example, in the simple case of tossing a coin, the expectation or prediction of heads turning up for 50% of the throws becomes increasingly accurate, as the number of tosses tends to infinity. When considering the thermodynamics of gases, Boltzmann recast the problem in terms of the statistical distribution of energy microstates ([Chap. 12](#)). Qualitatively this can be understood by imagining a large number of tiny sealed and evacuated cubical boxes (microstates), arranged in an orderly way within a very large cubical box (macrostate). Now consider that one of the tiny boxes is filled with warm air, impregnated with smoke (for the purposes of visualisation), and that once filled, and at equilibrium, tiny apertures are simultaneously, and instantaneously, opened between all the boxes. If the boxes were transparent we would observe the distribution of smoke spreading from one box to all boxes. This dissipation of the air through all the boxes represents growing entropy, which becomes a maximum when all boxes are equally filled and the system is again at equilibrium. The warm air in a single box is much more capable of doing ‘useful work’ than the cooler air distributed through all boxes.

The mathematics [11] which describes this process is replicated in Chap. 12, and it leads to the following well known (at least in the science and engineering communities) formula for entropy:

$$S = k \ln W \quad (1.6)$$

Here W is the number of possible realisations of the distribution $\{N_{xc}\}$ associated with a gas containing N molecules. $S = k \ln W$ is arguably one of the most important equations in physics, possibly ranking alongside $E = mc^2$. It is engraved on Boltzmann's tombstone in Vienna.

The Boltzmann equation for S permits a physical interpretation [11]. It suggests that each state or realisation of a gas of N molecules is a priori considered to occur equally frequently, or to be equally possible. For example, the highly ordered state in which all molecules in our multi-box system were located in one box at the same velocity (at equilibrium) is presumed to be just as possible, but less probable, to all subsequent states as the air leaks through the system. At the beginning just at the instant the apertures are opened, the denominator in the equation for W (Eq. 12.9) is equal to $N!$, which means that we must have $S = 0$. At any subsequent time the denominator has to be less than $N!$ and S increases monotonically as the logarithm of W . In a warm gas in which all molecules are in irregular thermal shuffling motion the equation predicts that the particle distribution will change inexorably to a form that accommodates more and more possible states which have similarly high probability. This, in turn, implies that, for a gas in a closed volume, entropy increases to a maximum. At this point equilibrium has been reached. This strategy of nature, does not just apply to gases, but to everything in the universe—hence the status which has been accorded to Boltzmann's equation. Imagine, for example, a well shuffled pack of playing cards. It is highly disordered and hence exhibits high entropy. Further shuffling will, in all probability, merely maintain the disorder and high entropy. The probability of a shuffle resulting in the cards being properly sequenced within their suits (high order; low entropy) is absolutely negligible. Boltzmann's interpretation of the second law is that an ordered closed system of low entropy will inexorably drift toward a state with higher probability; in other words, towards high entropy. Increasing entropy is essentially a measure of the growing degree of randomness inherent in a system. The second law is not absolute. It is possible for the entropy of a system to decrease, but not if it is 'closed' in the classical sense, as we shall see.

1.3.6 The Zeroth Law

That the zeroth law of thermodynamics is so called, is clearly an indication that while it was formulated subsequent to the announcement of the first and second laws, it is considered to provide a basic underpinning of, or platform for, these two laws. Scientists at the time of Clausius were quite unaware of any need to define temperature. It is probable that they considered it to be self-evident that the temperature of the heat sensitive constituent of a thermometer was the same as the

material or substance being measured. That they are in such equilibrium, is the defining property of temperature. At the interface between two different substances the temperature on one side of the interface must be equal to the temperature at the other: temperature is described as being continuous across the interface. Once it is appreciated that temperature is a measure of atomic or molecular velocities within a material or substance, this property is not difficult to comprehend. It has been termed the zeroth law of thermodynamics.

1.3.7 The Third Law

In the field of cryogenics, and in particular the nature of thermodynamics at temperatures close to absolute zero, the third law emerges. At very low temperatures atoms in a material find potential barriers very difficult to overcome because their thermal kinetic energies are so weak. For example hydrogen (H_2) can become liquid or even solid at low enough temperatures. At these temperatures the kinetic energies of the individual molecules are too weak to overcome the intermolecular forces. While hydrogen molecules are on average unpolarised, the positive charge of the nuclei can be temporarily displaced from the ‘centre of gravity’ of negative charge of the orbiting electrons, thus forming a short lived dipole. The electric attraction between these short lived dipoles (the Van der Waals force) is generally insignificant unless their kinetic energies are so low that the vibrating molecules cannot resist this force and begin adhering to each other. When this happens the gas becomes a liquid or a solid if the temperature is low enough. If the temperature approaches zero Kelvin, no potential barriers (Van der Waals attractive forces) no matter how small can be overcome, and this means that the material must assume the state of lowest possible energy. All molecular action ceases, and entropy must be zero. In theory volume also shrinks towards zero. But nothing can exist in zero volume, therefore zero temperature must be unachievable. This is the essence of the third law of thermodynamics. It is attributed to Hermann W. Nernst (1864–1941) who summarised the laws one to three of thermodynamics thus [11]:

It is impossible to build an engine that produces heat or work from nothing.

It is impossible to build an engine that produces work from nothing else than the heat of the environment.

It is impossible to take all the heat from a body.

1.4 The Quintessential Heat Engine

A heat engine typically uses energy to do work, provided in the form of a hot gas at a higher temperature than the environment in which the engine resides. In so doing the gas loses heat and its molecules eventually possess insufficient kinetic energy to continue to do useful work. At this stage it is then expelled through an exhaust. The first law and second law of thermodynamics provide the fundamental

constraints to the operation. The first law requires that the system should adhere to conservation of energy, while the second sets limits on the possible efficiency of the machine and determines the direction of energy flow.

1.4.1 Steam Engine

Heat engines such as steam engines and internal combustion engines in automobiles operate in a cyclic manner, with the reciprocating motion of a piston being converted to rotary motion by means of a mechanical connecting rod attached to the piston and a crank in the rotating shaft housing a flywheel. The hot gases are introduced into a cylinder which is swept by the piston, and thereby provide power to the device. In an ideal engine operating with an ideal gas the operation can be illustrated by means of a pressure–volume (PV) diagram as illustrated in Fig. 1.4. The hot gas is introduced into the cylinder when it is at its minimum volume position (1), at which point there is a very rapid increase in pressure (1–2) before the piston starts to move; in a steam engine by opening a steam valve, or in an internal combustion engine by igniting a charge of hydrocarbon vapour. This pressure is a manifestation of the incessant bombardment of the walls of the cylinder by highly agitated molecules of the hot gas. Each molecule exerts a force on the wall proportional to its change of momentum. When the pressure becomes high enough at (2) the piston begins to move and the cylinder volume increases (2–3). The gas does work on the piston which, with all its connecting parts, gains kinetic energy. The gas in the cylinder obviously expands and becomes less dense thus exerting less pressure on the walls and the piston. It also becomes cooler (refrigerator action), and the degree of cooling, for an ideal gas at least, can be estimated from application of Boyle’s law Eq. 1.3.

Once the piston reaches the end of its travel, a valve, or valves in the cylinder will be opened to exhaust the used gas. The pressure will drop almost instantaneously (3–4), and old gas will be ejected from the cylinder. On the return stroke (4–1) this gas will be compressed, in a simple single cylinder system by the force of inertia normally supplied by a fly-wheel. The cycle will then repeat.

Pressure–Volume (PV) diagrams are a primary visualization tool for the study of heat engines. Since the engines usually involve a gas as a working substance, the ideal gas law relates the PV diagram to the temperature so that the three essential state variables for the gas can be tracked through the engine cycle. Since work is done, only when the volume of the gas changes, the diagram gives a visual interpretation of the work done. Furthermore, the internal energy of an ideal gas depends upon its temperature, consequently the PV diagram, along with the temperatures calculated from the ideal gas law, determine the changes in the internal energy of the gas. Thus the amount of heat added can be evaluated from the first law of thermodynamics. In summary, the PV diagram provides the framework for the analysis of any heat engine which uses a gas as a working substance. For a cyclic heat engine process, the PV diagram will be closed loop.

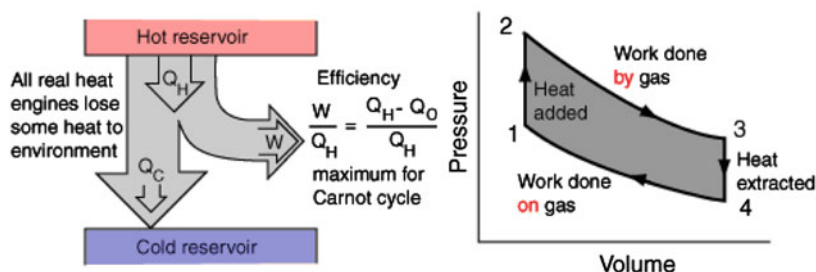


Fig. 1.4 Heat engine thermodynamics

The area inside the loop is a representation of the amount of work done during a cycle. Some idea of the relative efficiency of an engine cycle can be obtained by comparing its PV diagram with that of a Carnot cycle, the most efficient kind of heat engine cycle. A heat engine typically uses energy, provided in the form of heat, to do mechanical work, and then exhausts the cooler gases, which can no longer be used to do useful work within the engine. The relationship between heat and work can be studied by resorting to the science of thermodynamics. The first law and second law of thermodynamics constrain the operation of a heat engine. The first law is the application of conservation of energy to the system, and the second sets limits on the possible efficiency of the machine and determines the direction of energy flow.

A schematic, which is commonly used, sometimes in conjunction with a PV diagram, to illustrate the operation of a heat engine, is the energy reservoir model (Fig. 1.4). The engine takes energy from a hot reservoir and uses a portion of it to do work, but is constrained by the second law of thermodynamics to exhaust the remainder to a cold reservoir. In the case of the automobile engine, the hot reservoir is the burning fuel and the cold reservoir is the environment to which the combustion products are exhausted. The efficiency expression, given on the schematic, is a general one, but the maximum efficiency is limited to that of the Carnot cycle. This limitation is often called the thermal bottleneck.

1.4.2 Internal Combustion Engine

The internal combustion engine was first patented in 1861, but the first person to actually build a car with this engine was a German engineer named Nicolaus Otto (1832–1891). The four-stroke principle of operation is today commonly known as the Otto cycle and four-stroke engines using spark plugs are often referred to as Otto engines. The Otto cycle consists of (1) adiabatic compression, (2) heat

addition at constant volume, (3) adiabatic expansion and (4) rejection of heat at constant volume. The power delivered by the internal combustion engine originates primarily from the expansion of gases in the power stroke. Compressing the fuel and air into a very small space increases the efficiency of the power stroke (see [Chap. 14](#)), but at the expense of increasing the heating of the fuel as the mixture is more highly compressed. This has ramifications for cylinder head and valve design.

Diesel engines, invented by Rudolf Diesel (1858–1913], differ from Otto engines in that they rely on self-ignition, rather than spark ignition, for the engine to function. This engine solves several internal combustion engine problems associated with high compression. Firstly, air without fuel can be compressed to a very high degree without concern for self-ignition, and secondly the highly pressurized fuel in the fuel injection system cannot ignite without the presence of air.

A sample thermodynamic calculation for an internal combustion engine based on the Otto cycle is provided in [Chap. 14](#). Of course, modern engine design is today fully and accurately simulated in computer software, but it still remains useful (and most courses in thermodynamics would encourage students to do so) to perform ‘long hand’ calculations on idealised gas models in order to gain a thorough understanding of the thermodynamics.

The exposition of the operation of the fundamental heat engine, developed in this section, will provide a good platform, as we will see, for examining the Earth’s environmental ‘heat engine’, which may, or may not be controlled by a self-correcting ‘thermostat’, as is suggested by the Gaia Hypothesis. This contention is addressed in [Chap. 4](#).

References

1. Gregory MS (1971) History and development of engineering. Longman Group Ltd, London
2. Ruddiman WF (2003) The anthropogenic greenhouse era began thousands of years ago. *Clim Ch* 61:261–293
3. Ferguson N (2006) The ascent of money. Allen Lane Penguin Books, London
4. Porritt J (2007) Capitalism: as if the world matters. Earthscan, London
5. Northcott M (2004) An angel directs the storm: apocalyptic religion and american empire. I.B, Taurus, London
6. Mill JS (2004) A biography by Nicholas Capaldi. Cambridge University Press, Cambridge
7. Athanasiou A (1996) Slow reckoning. Secker & Warburg, London
8. Bakan Joel (2004) The corporation. Constable & Robinson Ltd., London
9. Asimov I (1975) Biographical encyclopaedia of science and technology. Pan Reference Books, London
10. Lavoisier AL (1965) Elementary treatise on chemistry. Dover Publications, New York Reprinted
11. Muller I (2007) A history of thermodynamics. Springer-Verlag, Berlin
12. Thurston RH (1960) Reflections on the motive power of fire. In: Sadi Carnot (ed). Other papers on the second law of thermodynamics. In: E. Clapeyron and R. Clausius. E. Mendoza (eds), Dover Publication, New York

13. Weinburg S (1993) *Dreams of a final theory*. Vantage, New York
14. Friedman M (2002) *Capitalism and freedom*. University of Chicago Press, Chicago
15. Cook E (1982) The consumer as creator: a criticism of faith in limitless ingenuity. *Energy Explor Exploitation* 1(3):189–201
16. Joule JP (1857) Remarks of the heat and constitution of elastic fluids. *Philosophical Mag Series IV*(XIV):211